RE-ORDER NO. 63-187

G. T. SCHJELDAHL COMPANY

NORTHFIELD, MINNESOTA

January 30, 1963

FINAL REPORT

EVALUATION OF THE COMPATIBILITY OF POLYVINYLIDENE FLUORIDE (KYNAR) WITH STORABLE LIQUID PROPELLANTS (NITROGEN TETROXIDE AND HYDRAZINE)

Prepared for

Jet Propulsion Laboratory
California Institute of Technology
under
Contract No. NI-120421

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I. SUMMARY

This final report presents the result of research conducted under the Jet Propulsion Laboratory's Contract No. NI-120420. The objective of this contract was the evaluation of polymeric materials potentially usable to construct expulsion membranes for storable liquid propellants such as nitrogen tetroxide and hydrazine. The material studied was polyvinylidene fluoride available as Kynar from Pennsalt Chemical Company.

The work of others has been reviewed and applied to this study and the aid of materials suppliers has been enlisted whenever possible. The study of polymers was deviated from, in one respect, when some aluminum laminates were prepared for a brief evaluation at Jet Propulsion Laboratory.

The evaluation accomplished at the Schjeldahl Company has been based on 1) preparation of film samples from resins and from resin dispersions and solutions, 2) immersion tests in storable propellants, followed by measuring physical properties of the films and resins, 3) simple permeability tests. In all tests comparison samples of other resin systems were included.

Work since the last formal report has centered around long-term immersion studies and determining polyvinylidene fluoride film characteristics after orienting and stretching procedures.

II. CONCLUSIONS

1. The polyvinylidene fluoride polymer is unattached chemically by N_2O_4 or Hydrazine. Swelling occurs with N_2O_4 and some brittleness develops on long contact with hydrazine.

2. Solution cast and extrusion were demonstrated for the preparation of film from polyvinylidene fluoride. Sintering of solid material by a fluidized bed technique showed little promise.

3. The suitability of using infrared spectral analysis for establishing physical and chemical interaction between propellant and selected film was demonstrated.

4. The testing conducted with polyvinylidene fluoride and Teflon FEP indicated promise for the former for use in applications of intermittant exposure or where permeability is not an important factor. Consideration should, therefore, be given to its use in O-rings, gaskets, or molded parts.

5. Evidence was obtained to indicate that polyvinylidene fluoride films can be oriented by application of strain at a proper temperature. Sensitivity of the material to melt fracture and to temperature are sufficiently great to indicate that operation within very narrow limits will be necessary.

6. The test methods were suitable for preliminary testing or screening of materials but refinements are needed for definition of long-term behavior of material in contact with storable propellants.

7. Studies of the effect of propellant on polymer molding powder in comparison with biaxially oriented film indicate that the orientation process may reduce susceptibility to attack several fold..

Recommendations:

It is recommended that:

1. Polyvinylidene fluoride be considered for systems involving N_2O_4 where a relatively hard polymer with some permeability is suitable. (Performance anticipated would be equivalent or superior to that of Teflon FEP)

2. Vinylidene fluoride be considered for use in cross-linked polymer systems where resistance to N_2O_4 is important. (The absence of chemical attack and the low order of swelling, point to an excellent potential for reduced swelling. Complete elimination of permeability is not to be anticipated.)

3. Vinylidene fluoride polymers be considered for use in laminated systems where metals are employed to eliminate permeability. (The resistance of the few aluminum laminates prepared with epoxy adhesives under this program indicates the effectiveness of metal barriers for N_2O_4).

III. TECHNICAL DISCUSSION

Through May 1961, work under the contract centered on a brief review of the work of others in the area of storable propellants compatability. Kynar, vinylidene fluoride, being newly available and promising in preliminary experiments at G. T. Schjeldahl Company was the subject of emphasis. The potential promised that vinylidene fluoride would be comparable to Teflon FEP in compatability. Suppliers technical product development personnel were interviewed to establish a justification for the study of Kynar as a propellant barrier material. (1)

Following this, a group of materials required for the study was assembled (cylinder N_2O_4, anhydrous hydrazine, and apparatus). Initial attempts to prepare Kynar film samples were made. Very thin films (0.0005-inch) were cast continuously, heavier sections (0.001- 0.003-inch) were cast in small areas, and plaques (0.25-inch) were compression molded. The greatest difficulties occured in preparing a uniform plaque, and completely removing the high boiling-point solvents and dispersants used in casting. These samples were, in several ways, exposed to nitrogen tetroxide and hydrazine.

In the period covered by the second report (2) emphasis was again placed on Kynar. Polypropylene, polycarbonate, polyvinylidene chloride polymer and polyethylene were included

in initial immersion tests for comparison. The polyethylene and and polycarbonate were attacked on initial immersion in propellants, the polycarbonate being completely decomposed. Films of vinylidene fluoride, vinylidene chloride, and polypropylene were immersed and, on removal, tested for tensile strength, inspected for discoloration (indicating absorption) and the infrared spectra recorded to check for residual solvents and for nitration of the polymer.

The polyvinylidene fluoride films would discolor on immersion but on exposure to air would lose the color. No infrared absorption bands indicated nitration of the polymer. It was noted then that the spectra indicated residual solvents and dispersants. It was assumed that these residuals could have left material which would readily transmit the nitrogen tetroxide. The polypropylene was observed to suffer greater attack on the molding pellets than on the oriented film. After one week, an infrared absorption band indicated some nitration. A 2-oz Boston round bottle of nitrogen tetroxide exuded the material through the wall after a few days. Following this, simple permeation and longer-term and higher temperature immersion tests were run.

The third letter report (3) described simple permeation testing and some 150 F nitrogen tetroxide immersion tests in addition to those already run. At this time, the seemingly delayed attack on biaxially-oriented film compared to polypropy-

lene pellets was noted. Polyvinyl fluoride, polyvinyl chloride copolymer, and polypropylene films and pellets were sealed into glass tubes (15 mm tubes for room temperature, 8 mm tubes for 150 F). After one to two days, the polypropylene pellets at 150 F degraded enough to burst the sample tube. After two to seven days, the biaxially-oriented polypropylene film samples burst the sample tube. (After roughly three months, the polypropylene samples immersed at room temperature burst their sealed tubes.) The vinylidene chloride copolymer and the vinylidene fluoride would regain original physical properties within a day after being removed from the nitrogen tetroxide. Simple permeability studies were made to compare the polyvinylidene film to Teflon FEP. The permeability is almost equal to that of Teflon FEP of similar thicknesses. The immersion and permeability samples of Kynar were prepared from six pounds of film extruded experimentally at the Panelyte division of St. Regis Paper Company at Richmond, Indiana. This eliminated inconsistancies in the sample but it also introduced the problem of melt fractures in the film and very low tensile strength and elongation in the transverse direction of the film.

Long-term exposures were then initiated for the polyvinylidene fluoride and the polyvinylidene chloride polymer in both hydrazine and N_2O_4 sealed in tubes. These sealed tubes have been maintained at room temperature for 13 months.

For two months some small diameter tubes containing N_2O_4 and samples of Kynar and vinylidene chloride copolymer were held at 150 F. Corresponding samples of polypropylene film and resin burst the containing tube. The vinylidene chloride copolymer was degraded and became flaky when removed from the 150 F immersion in N_2O_4. The Kynar film samples, after being exposed to air for three days had tensile properties approximately the same as control sample. The sample was bleached to a hazy water-white material. It was apparent that in this case N_2O_4 was absorbed in the film. There was not any indication of nitration of the Kynar. Samples of room temperature immersion in hydrazine were yellowed and embrittled slightly after 13 months.

Repeated attempts were made to obtain biaxially oriented Kynar film to evaluate the effect of orientation on permeability. The Kynar film has poor hot strength and all stretching took place from a line of melt fracture. In the extruded film this was always in the machine direction. Within the Schjeldahl Company, the stretching was attempted by drawing in one direction in a frame in the tensile tester, drawing over a sphere (thermoforming) and by pressing between hot platens. None of these systems offered a suitable sample. The T. M. Long Company, Summerville, New Jersey offered to stretch limited samples.

The film was described by them as being sensitive in one direction and not lending itself to good stretching on the T. M. Long film stretcher. For this reason, the stretched film samples were not of a quality suitable for use as permeability test specimens.

IV. RESULTS OF TEST PROGRAMS

The first phase of the work resulted in confirmation of the choice of Kynar as a potential material. The justification is reviewed in the notes of the meeting with Dr. Barnhart of Pennsalt Chemicals Corporation. Dr. Barnhart offered a great deal of information on the handling properties and chemical nature of Kynar. A review with Plastec (Picatinney Arsenal) of an Aerojet General report on the evaluation of elastomeric compounds for use with storable propellants was not entirely applicable because it was concerned more with brief exposure and intermittant service. This report did indicate that Teflon and hexamethylene diamine Nylons are potentially usable but that Teflon usefulness lay in its ability to degas easily what it had absorbed.

During the second phase, films of polyvinylidene fluoride were cast from Kynar dispersions and solutions. It was noted that one could observe residual solvent readily in the infrared spectra of the films. A dispersion of powder in a 80/20 blend of dimethylphthalate and diisobutyl ketone offered some thixotropy and could be considered to stop the running problem experienced when continuous films were cast on the Schjeldahl laminator. Physical properties of Kynar films prepared in this manner were essentially the same as those published earlier.

Initial immersion testing eliminated polycarbonate and vinyl acetate. Polypropylene was later eliminated when higher temperatures (150 F) were used. The spectra of all material samples immersed

in N_2O_4 showed on absorption band at 1550 cm^{-1} which diminished with time. This indicated that absorbed N_2O_4 would be completely released on degassing.

It was noted that biaxially oriented polypropylene sheet was less sensitive to N_2O_4 degradation than were polypropylene pellets. After 1 week immersion, a permanent absorption band at 1550 cm^{-1} indicated nitration of polypropylene. Initial permeability tests indicated leakage rather than permeability.

In the third phase of the study, immersion of samples in nitrogen tetroxide was done at 150 F. Polypropylene pellets would break the sample-containing tube in less than 24 hours. Oriented polypropylene film took 48 hours to burst tne tube. The Kynar film discolored, indicating absoption. After brief exposure to air, the Kynar films regained original properties. The properties, if tested before degassing could occur, were

Ultimate Tensile	73 % of original
Ultimate Elongation	10 % of original
Color	Green from original tan.

A sample polyvinylidene fluoride film prepared outside the Schjeldaal Company showed leakage. The high melt viscosity forced open the extruded sheet die to three times original depth. Poor hot strength was observed. Annealing of the sample did little to diminish the effects of melt fracture at the extruder die.

Experimental work has substantiated the difficulty of biaxially orienting Kynar film. Hot stretching in a frame, in the tensile tester, and by drawing over a dome would not stretch the film uniformly. The T. M. Long Company also noted the poor hot strength and the melt fracture problem.

Permeability measurements of Kynar film gave the following results:

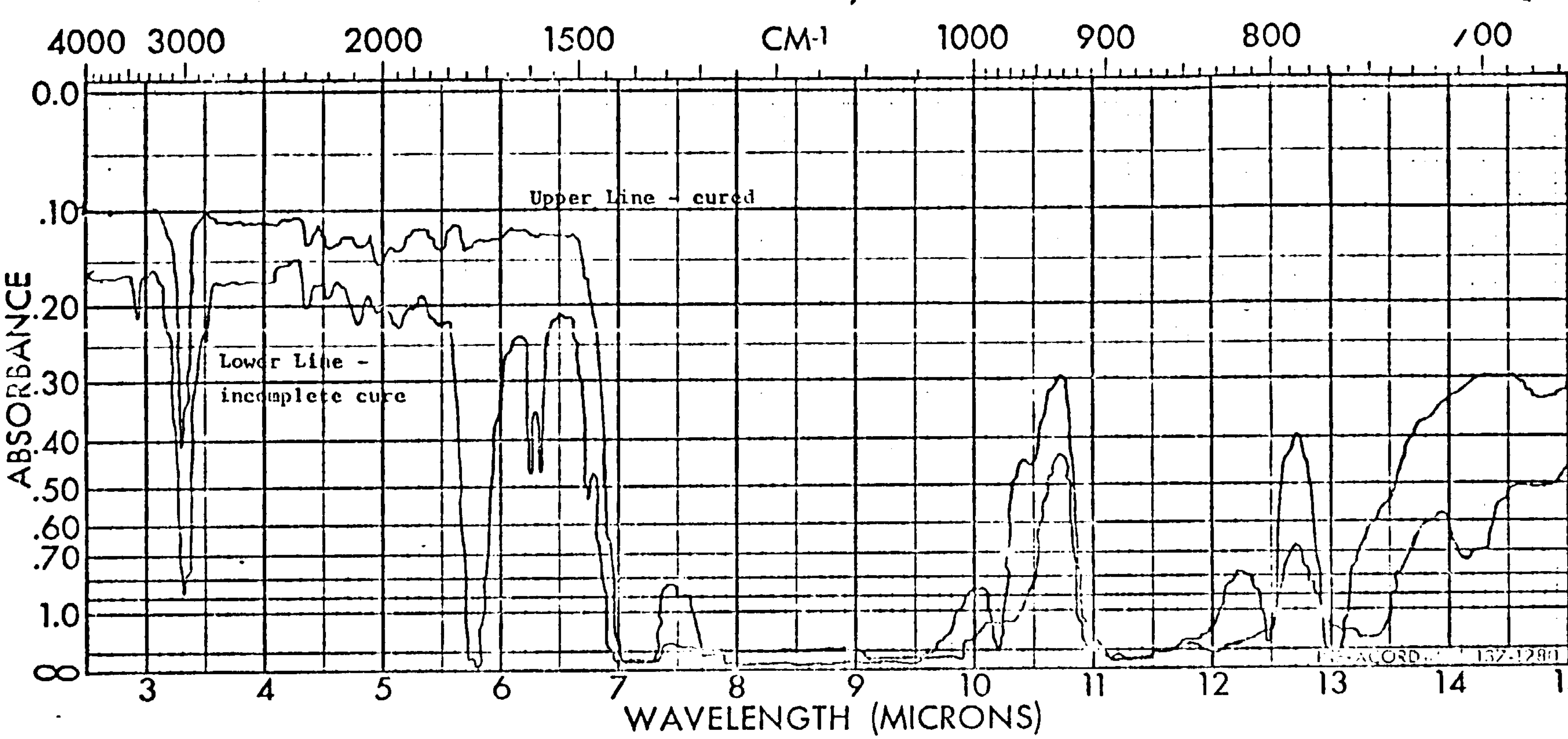
Length of Exposure (Hrs)	Description of Film	Permeability mg/(mil)(day)(atm)(in^2)
48	7-mil Kynar	95
100	7-mil Kynar	100
21	7-mil Kynar	160
21	5-mil Teflon FEP(Control)	95

Long-term (13 months) immersion of samples in N_2O_4 and N_2H_4 was carried out. After removal from these conditions, the Kynar film was bleached white by N_2O_4 and stained yellow by the N_2H_4. The hydrazine also made the film more brittle. Polypropylene was no longer of interest in higher temperature immersion as reaction had already been shown to occur. The vinylidene chloride copolymer was embrittled seriously by the N_2O_4.

GENERAL RESULTS TABLE

	Polyvinylidene fluoride*	Polyvinylidene chloride	Teflon FEP	Polypropylene	Vinyl Acetate	Polycarbonate
Brief Exposure to N_2O_4	Not Affected	Not Affected	Not Affected	Discolored	Decomposed	Decomposed
2 months exposure to N_2O_4	Absorbed Discolored No permanent effect			Tank Rupture		
13 months in N_2O_4	Absorbed, softened, bleached - no chemical reaction - no effect on tensile strength	Absorbed, some chemical reaction dis-colored, very brittle	Absorbed, swelled - no chemical reaction	Decomposed		
Brief exposure to Hydrazine	Not Affected	No data	Not Affected	No data	No data	No data
Long term exposure to Hydrazine	Embrittled, discolored	No data	No data			

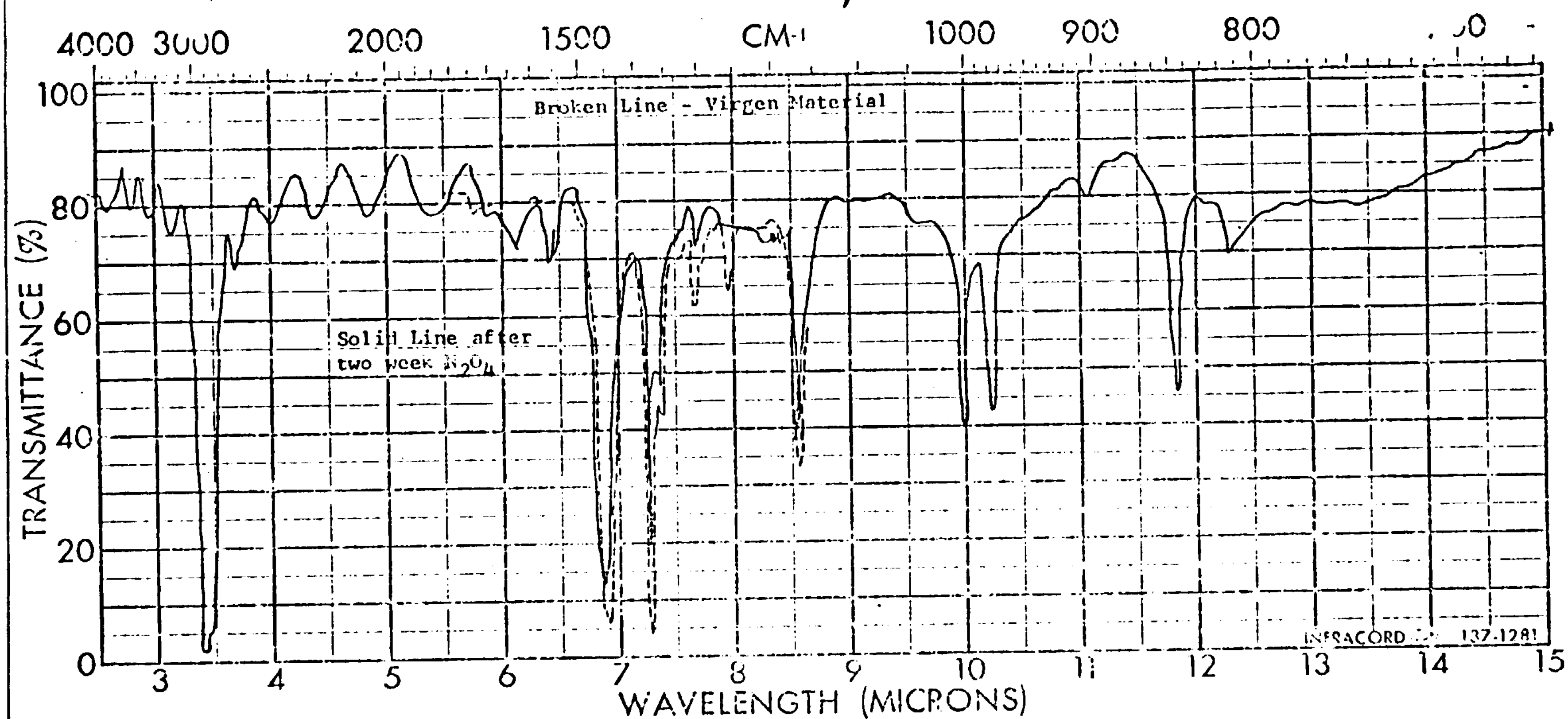
* Extruded Film Sample



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS line at 1700
SAMPLE Kynar film	Pennsalt	1. Upper line - cured	and doubled at 1600 cm^{-1}
comparison of incomplete	PURITY from dispersion 18	2. Lower line - incomplete cure	indicate DM phthalate
cures	PHASE film	DATE August 2, 1961	retention
	THICKNESS 2+ mils	OPERATOR Herb Fick	

SPECTRUM NO.
SAMPLE

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. x	ORIGIN Montecatini	LEGEND	REMARKS
SAMPLE Montecatini		1. Broken Line - Virgen Material	Possible absorption for NO_2
Polypropylene after	PURITY Sample	2. Solid Line after 2 weeks N_2O_4	peak @ 1560. 1370 is masked
2 week immersion in N_2O_4	PHASE Film	DATE July 5, 1961	compare to Spectra 69
	THICKNESS 1 mil	OPERATOR Herb Fick	

SPECTRUM NO.
SAMPLE

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

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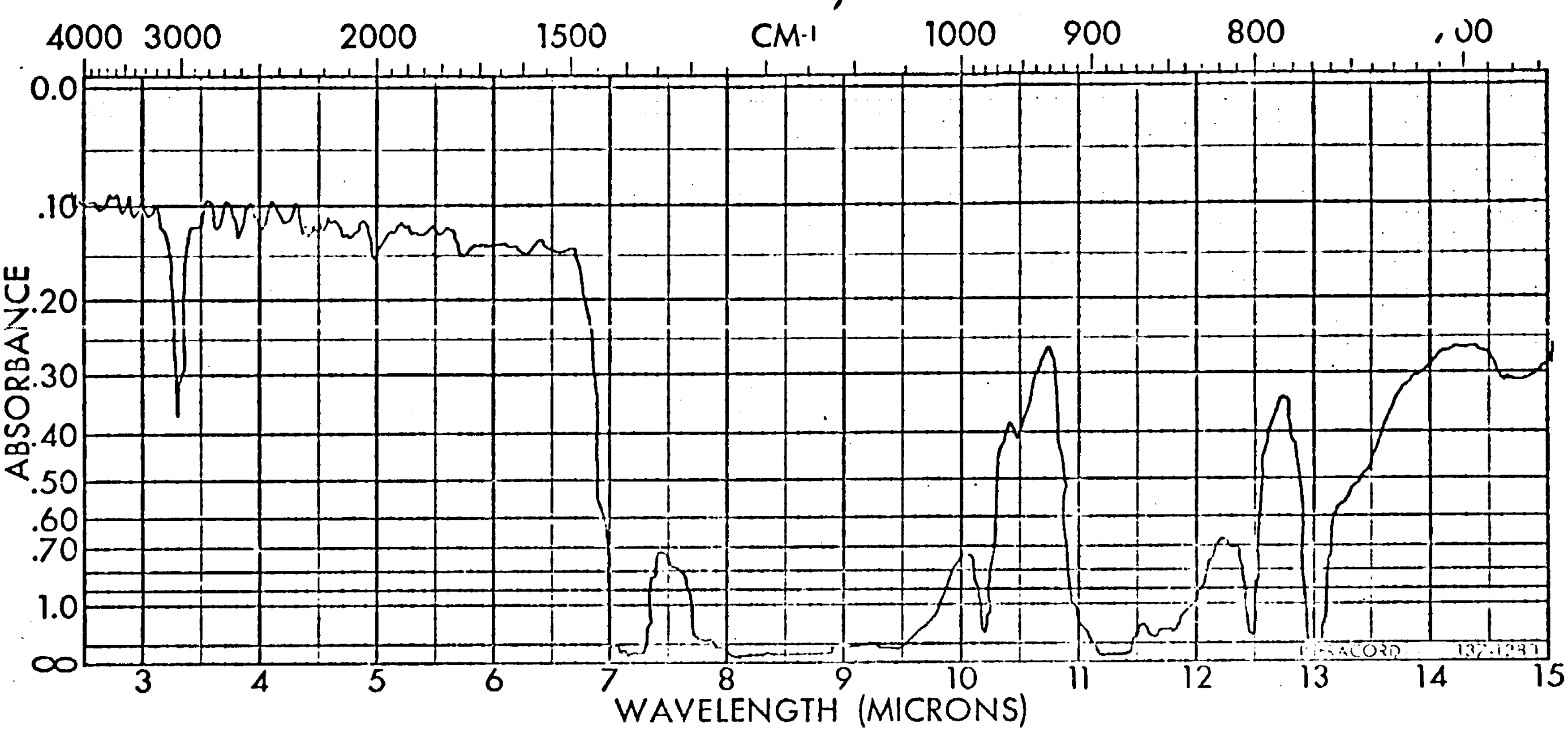

SPECTRUM NO.	ORIGIN Pennsalt Dispersion	LEGEND	REMARKS
SAMPLE Kynar		1.	no 1700 or 1550 absorption
after 1 month in N_2O_4	PURITY film	2.	Sample allowed to lose
permeability app.	PHASE	DATE August 2, 1961	absorbed N_2O_4
	THICKNESS	OPERATOR Herb Fick	

SPECTRUM NO.
SAMPLE

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

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References

1. Letter to R. N. Porter - Jet Propulsion Laboratory, May 27, 1961
2. Letter to R. N. Porter - Jet Propulsion Laboratory, August 4, 1961
3. Letter to R. N. Porter - Jet Propulsion Laboratory, November 3, 1961
4. Proposal to Jet Propulsion Laboratory, February 6, 1961
5. Anonymous - Allied Chemical Company product bulletin Nitrogen Tetroxide

Amberg, L.O., Robinson, A.E. - Ethylene-propylene rubber I & EC 53 5(1961)

Baldrige, John H. - Determining Capability of Elastomers with Liquid and Gaseous Rockett Propellant, Joint Army, Navy, Air Force Conference on Elastome Development and Research, Oct. 1958

Barnhart, Ferren, Iserson - Polyvinylidene Fluoride, Vol VII Society of Plastics Enginner, ANTEC Paper, Jan. 1961

Capron, Dukert, Robb - Polyvinylidene Fluoride, Society of Plastics Engineers, ANTEC Paper, Jan. 1961

Liberto, Ralph R. - Storable Propellant Data for Titan II Program, Contract No. AF 04 (611) 6079, Project 6753 Task 30282 AFFTC TR-60-62

Riebsomer, J.L. - The reactions of Nitrogen Tetroxide with Organic Compounds. Allied Chemical Corporation

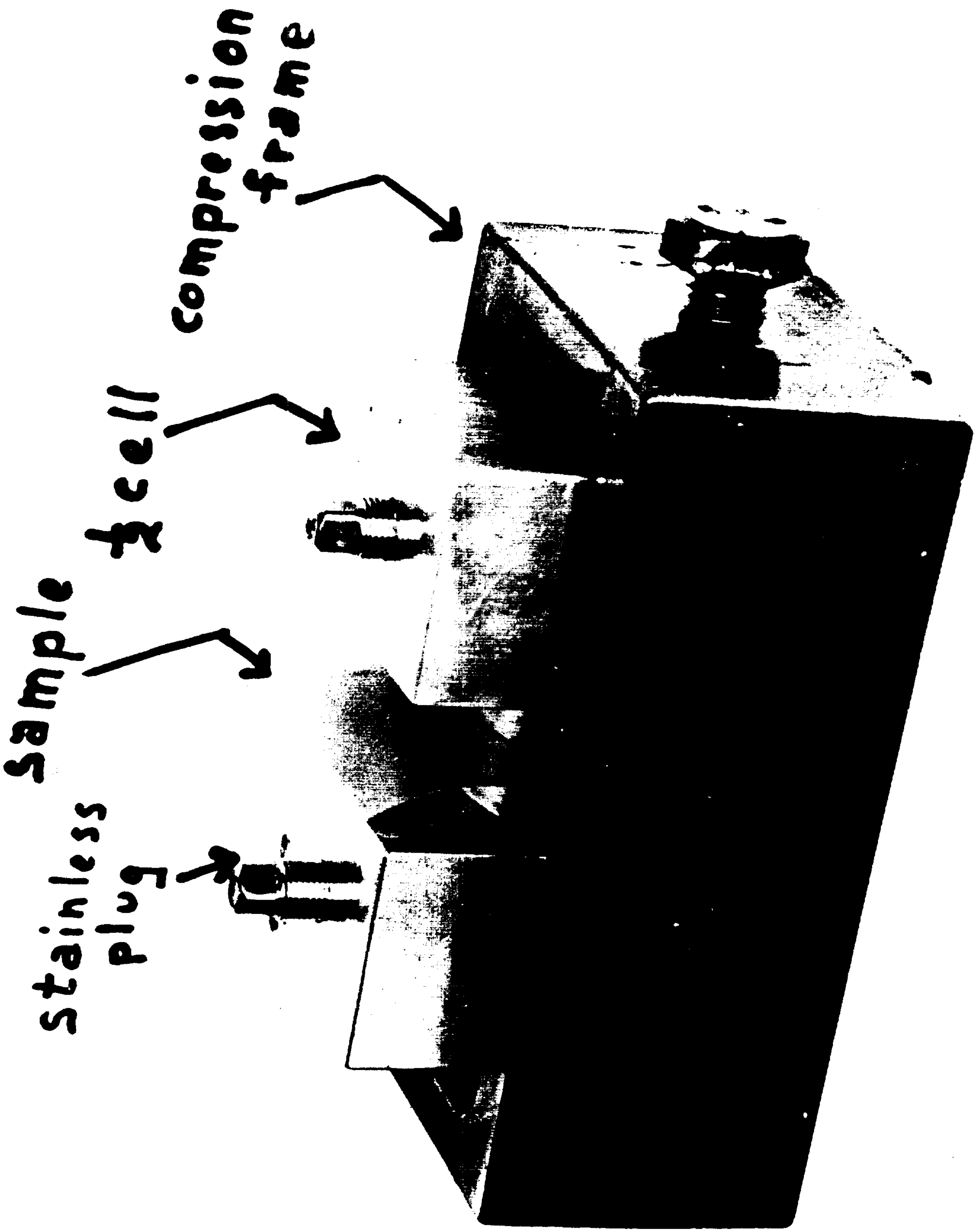
Stainless plug
Sample
℄ cell
Compression frame

TABLE II
PHYSICAL PROPERTIES OF KYNAR GRADE 18

Property	Measurement	Unit	ASTM No.
Clarity	transparent to translucent		
Melting point, crystalline	340	°F	
Specific gravity	1.76		D792
Specific volume	15.7	in^3/lb	
Refractive index, n_D^{25}	1.42		D542
Molding temperatures	400-550	°F	
Mold shrinkage, average	0.020	in/in	
Color possibilities	unlimited		
Machining qualities	excellent		
Flammability	self-extinguishing, non-dripping		
Tensile strength, 77°F	7000	psi	D638
Tensile strength, 212°F	5000	psi	D638
Elongation, 77°	300	percent	D638
Elongation, 212°F	400	percent	D638
Yield point, 77°F	5500	psi	D638
Yield point, 212°F	2500	psi	D638
Creep, 2000 psi, 77°F, 10,000 hrs. *See Figure 1*	0.02	in/in	
Compressive strength, 77°F	10,000	psi	D695
Modulus of elasticity, 77°F			
in tension	1.2×10^5	psi	D638
in flexure	2.0×10^5	psi	D790
in compression	1.2×10^5	psi	D695
Izod impact, notched, 77°F	3.8	ft-lb/in	D256
Izod impact, unnotched, 77°F	30	ft-lb/in	D256
Durometer hardness	80	Shore, D scale	
Heat distortion temperature, 66 psi	300	°F	D648
Heat distortion temperature, 264 psi	195	°F	D648
Abrasion resistance, Tabor CS-17, ½ kg load	17.6	mg/1000 cyc	
Coefficient of sliding friction to steel	0.14-0.17		
Thermochemical properties (estimated)			
$1/n\ (CH_2CF_2)_n \rightarrow CH_2CF_2(g)\ \Delta H^\circ_{298}$	+41.2	kcal	
$1/n\ (CH_2CF_2)_n \rightarrow 2C + 2HF(g)\ \Delta H^\circ_{298}$	−12.0	kcal	
Thermal coefficient of linear expansion *See Figure 2*	8.5×10^{-5}	1/°F	D696
Thermal conductivity (Room temperature to 325°F)(2)	0.14-0.11	BTU/hr-ft-°F	
Specific heat	0.33	BTU/lb-°F	
Thermal degradation temperature	>600	°F	
Low temperature embrittlement	< −80	°F	
Water absorption	0.04	percent	D570
Moisture vapor permeability	1.0	$g/mil\text{-}24\ hr\text{-}m^2\text{-}atm$	
Radiation resistance (Co^{60})	$>300 \times 10^6$	roentgens	

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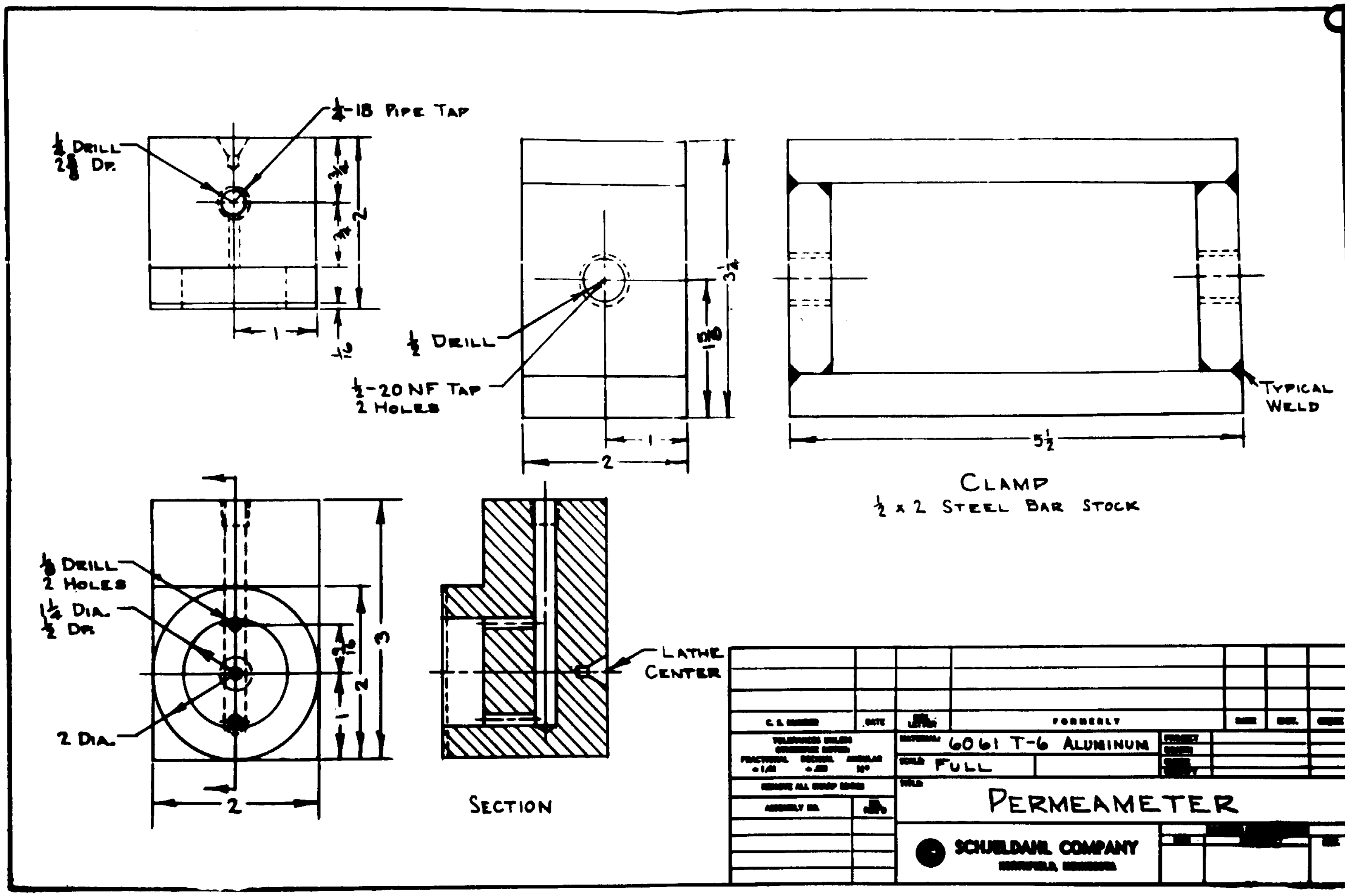
TABLE III
CHEMICAL RESISTANCE OF KYNAR

Tensile strength of 5 mil. film immersed for 30 days at 122°F. in various chemical compounds. Unexposed control specimen tensile strength is 7200 psi.

	Chemical Compound	Tensile After Exposure (psi)
Acids:	Sulfuric, fuming	degraded
	Sulfuric, 95%	7100
	Nitric, fuming	6300
	Acetic, glacial	5400
	Hydrochloric 35%	7100
	Sulfuric/hydrochloric 50/50	7300
	Phosphoric 85%	7200
	Formic	6800
	Hydrofluoric 28%	6700
	Monochloroacetic	5400
Bases:	Sodium hydroxide 50%	7200
	Ammonium hydroxide	7200
	Diethylamine	5500
	Triethylamine	6400
	n-Butylamine	degraded
	Aniline	5400
	Monoethylaniline	5600
	Pyridine	4900
	Hydrazine hydrate	7200
	Hydrazine	5800
	Unsymmetrical dimethylhydrazine	4700
Organic Compounds:	n-Heptane	6500
	Isooctane	6000
	Kerosene	7100
	Benzene	5600
	Toluene	5900
Organic Compounds: (Contd.)	Carbon tetrachloride	6700
	Trichloroethylene	6700
	Ethylene dibromide	6500
	o-Dichlorobenzene	6200
	Chlorofluoroalkanes (e.g. Isotron® 113)	6900
	Ethanol	6000
	Ethylene glycol	7100
	Phenol	5700
	Ethyl acetate	5000
	Acetone	partially dissolved
	Acetophenone	5400
	Acetaldehyde	5200
	Benzaldehyde	5000
	Furfural	5000
	Dioxane	5200
	Nitrobenzene	5000
	Dimethylsulfoxide	partially dissolved
	Dimethylacetamide	partially dissolved
Other Chemicals:	Chlorine (dry, 77°F)	7000
	Chlorine (wet)	7100
	Bromine (dry, 77°F)	6700
	Phosphorus oxychloride	4800
	Dinitrogen tetroxide	6500
	Hydrogen peroxide (90%, 77°F)	5500



1/4-18 Pipe Tap
1/4 Drill 2 5/8 Dp.
1/2 Drill
1/2-20 NF Tap 2 Holes
Clamp
1/2 x 2 Steel Bar Stock
Typical Weld
5 1/2
1/8 Drill 2 Holes
1 1/4 Dia. 1/2 Dp.
2 Dia.
Lathe Center
Section
6061 T-6 Aluminum
Full
Permeameter
Schjeldahl Company